

ATTACHMENT N

CONFIRMATORY VOLATILE ORGANIC COMPOUND MONITORING PLAN

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Acronyms and Abbreviations

BFB	4-Bromofluorobenzene
BS/BSD	blank spike/blank spike duplicate
CH	Contact-handled
CLP	Contract Laboratory Program
COC	concentration of concern
CRQL	contract-required quantitation limit
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ft	feet
FTIR	Fourier transform infrared spectrometry
g/mol	grams per mole
GC/MS	gas chromatography/mass spectrometry
HWDU	Hazardous Waste Disposal Unit
LCS	laboratory control sample
m	meter
MDL	method detection limit
MOC	Management and Operating Contractor (Permit Condition I.D.3)
MRL	method reporting limit
NIST	National Institute of Standards and Testing
NMAC	New Mexico Administrative Code
ppbv	parts per billion by volume
QA	quality assurance
QAPD	Quality Assurance Program Description
QAPjP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
SOP	standard operating procedure
SOW	statement of work
TIC	tentatively identified compound
TRU	Transuranic
VOC	volatile organic compound

WIPP Waste Isolation Pilot Plant

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ATTACHMENT N

CONFIRMATORY VOLATILE ORGANIC COMPOUND MONITORING PLAN

N-1 Introduction

This Permit Attachment describes the confirmatory monitoring plan for volatile organic compound (**VOC**) emissions from mixed waste that may be entrained in the exhaust air from the U.S. Department of Energy (**DOE**) Waste Isolation Pilot Plant (**WIPP**) Underground Hazardous Waste Disposal Units (**HWDUs**) during the disposal phase at the facility. The purpose of the confirmatory VOC monitoring is to confirm that the concentrations of VOCs in the emissions from the Underground HWDUs do not exceed the VOC room-based limits specified in Permit Module IV. This plan includes the monitoring design, a description of sampling and analysis procedures, quality assurance (**QA**) objectives, and reporting activities.

N-1a Background

The Underground HWDUs are located 2,150 feet (ft) (655 meters [m]) below ground surface, in the WIPP underground. As defined for this Permit, an Underground HWDU is a single excavated panel consisting of seven rooms and two access drifts designated for disposal of contact-handled (**CH**) transuranic (**TRU**) mixed waste. Each room is approximately 300 ft (91 m) long, 33 ft (10 m) wide, and 13 ft (4 m) high. Access drifts connect the rooms and have the same cross section. The Permittees shall dispose of TRU mixed waste in Underground HWDUs designated as Panels 1 through 7.

This plan addresses the following elements:

1. Rationale for the design of the monitoring program, based on:

- Possible pathways from WIPP during the active life of the facility
- VOC sampling operations at WIPP
- Optimum location of the ambient mine air monitoring stations

2. Descriptions of the specific elements of the monitoring program, including:

- The type of monitoring conducted
- The location of the monitoring stations
- The monitoring interval
- The specific hazardous constituents monitored
- The implementation schedule for the monitoring program
- The equipment used at the monitoring stations
- Sampling and analytical techniques used
- Data recording/reporting procedures

The results of baseline VOC monitoring at WIPP were used, in part, to define the confirmatory monitoring program that will be established for the Disposal Phase, during which full-scale

waste emplacement activities will occur. The baseline VOC monitoring results were presented in Appendix D21 of the WIPP Resource Conservation Recovery Act (**RCRA**) Part B Permit Application (DOE, 1997). These data represent the anticipated background levels of VOCs during operations at WIPP.

N-1b Objectives of the Confirmatory Volatile Organic Compound Monitoring Plan

The CH TRU mixed waste disposed in the WIPP Underground HWDUs contain VOCs which could be released from open and closed panels located at WIPP during the disposal phase of the project. This plan describes how VOCs released from waste panels will be monitored to confirm that the annual average concentration of VOCs in the air emissions from the Underground HWDUs do not exceed the VOC concentrations of concern (**COC**) listed in Table N-2.

N-2 Target Volatile Organic Compounds

The target VOCs for this sampling plan will be as follows:

- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- 1,1-Dichloroethylene
- 1,2-Dichloroethane
- Methylene chloride
- 1,1,2,2-Tetrachloroethane
- Toluene
- 1,1,1-Trichloroethane

These target VOCs were selected because together they represent approximately 99 percent of the risk due to air emissions. Physical and chemical data for these target VOCs for confirmatory air monitoring are presented in Table N-1.

N-3 Monitoring Design

Detailed design features of this plan are presented in this section. This plan uses available sampling and analysis techniques to measure VOC concentrations in air. Available sampling equipment includes the WIPP VOC canister samplers.

N-3a Sampling Locations

The initial configuration for the confirmatory VOC monitoring stations is shown in Figure N-1. All mine ventilation air which could potentially be impacted by VOC emissions from the Underground HWDUs identified as Panels 1 through 7 will pass monitoring Station VOC-A, located in the E-300 drift as it flows to the exhaust shaft. Air samples will be collected at two locations in the facility to quantify airborne VOC concentrations. VOC concentrations attributable to VOC emissions from open and closed panels containing CH TRU mixed waste will be measured by placing one VOC monitoring station just downstream from Panel 1 at VOC-A. The location of Station VOC-A will remain the same throughout the term of this Permit. The

second station (Station VOC-B) will always be located upstream from the open panel being filled with waste (starting with Panel 1 at monitoring Station VOC-B (Figure N-1). In this configuration, Station VOC-B will measure VOC concentrations attributable to releases from the upstream sources and other background sources of VOCs, but not releases attributable to open or closed panels. The location of Station VOC-B will change when disposal activities begin in the next panel. Station VOC-B will be relocated to ensure that it is always upstream of the open panel that is receiving TRU mixed waste. Station VOC-A will also measure upstream VOC concentrations measured at Station VOC-B, plus any additional VOC concentrations resulting from releases from the closed and open panels. A sample will be collected from each monitoring station on designated sample days. For each quantified target VOC, the concentration measured at Station VOC-B will be subtracted from the concentration measured at Station VOC-A to assess the magnitude of VOC releases from closed and open panels.

The sampling locations were selected based on operational considerations. There are several different potential sources of release for VOCs into the WIPP mine ventilation air. These sources include incoming air from above ground and facility support operations, as well as open and closed waste panels. In addition, because of the ventilation requirements of the underground facility and atmospheric dispersion characteristics, any VOCs that are released open or closed panels may be difficult to detect and differentiate from other sources of VOCs at any underground or above ground location further downstream of Panel 1. By measuring VOC concentrations close to the potential source of release (i.e., at Station VOC-A), it will be possible to differentiate potential releases from background levels (measured at Station VOC-B).

N-3b Analytes to Be Monitored

The nine VOCs that have been identified for monitoring are listed in Table N-1. The analysis will focus on routine detection and quantification of these compounds in collected samples. Other compounds may also be present in the samples. As part of the analytical evaluations, the presence of other compounds will be investigated. The analytical method will allow semiquantitative evaluation of these compounds as tentatively identified compounds.

N-3c Sampling and Analysis Methods

The present WIPP VOC monitoring program includes a comprehensive VOC monitoring program established at the facility; equipment, training, and documentation for VOC measurements are already in place.

The method that will be used for VOC sampling is based on the concept of pressurized sample collection contained in the U.S. Environmental Protection Agency (**EPA**) Compendium Method TO-14A (EPA, 1997). The TO-14A sampling concept uses 6-liter SUMMA[®] passivated stainless-steel canisters to collect integrated air samples at each sample location. This conceptual method will be used as a reference for collecting the samples at WIPP. The samples will be analyzed using gas chromatography/mass spectrometry (**GC/MS**) under an established QA/quality control (**QC**) program. Laboratory analytical procedures have been developed based on the concepts contained in both TO-14A and the draft *EPA Contract Laboratory Program - Statement of Work (CLP-SOW) for Volatile Organics Analysis of Ambient Air in Canisters* (EPA, 1994). Section N-5 contains additional QA/QC information for this project.

1 The TO-14A method is an EPA-recognized sampling concept for VOC sampling and speciation.
2 It can be used to provide integrated samples, or grab samples, and compound quantitation for a
3 broad range of concentrations. The sampling system can be operated unattended but requires
4 detailed operator training.

5 The field sampling systems will be operated in the pressurized mode. In this mode, air is drawn
6 through the inlet and sampling system with a pump. The air is pumped into an initially evacuated
7 SUMMA[®] passivated canister by the sampler, which regulates the rate and duration of sampling.
8 The passivation process forms a pure chrome-nickel oxide on the interior surfaces of the
9 canisters. By the end of each sampling period, the canisters will be pressurized to about two
10 atmospheres absolute. In the event of shortened sampling periods or other sampling conditions,
11 the final pressure in the canister may be less than two atmospheres absolute. Sampling
12 duration will be approximately six hours, so that a complete sample can be collected during a
13 single work shift.

14 The canister sampling system and GC/MS analytical method are particularly appropriate for the
15 VOC Confirmatory Monitoring Program because a relatively large sample volume is collected,
16 and multiple dilutions and reanalyses can occur to ensure identification and quantification of
17 target VOCs within the working range of the method. The contract-required quantitation limits
18 (**CRQL**) proposed by the EPA in the CLP-SOW are 5 parts per billion by volume (**ppbv**) or less
19 for the nine target compounds (EPA, 1994). Consequently, low concentrations can be
20 measured. CRQLs are the EPA-specified levels of quantitation proposed for EPA contract
21 laboratories that analyze canister samples by GC/MS. For the purpose of this plan, the CRQLs
22 will be defined as the method reporting limits (**MRL**). The MRL is a function of instrument
23 performance, sample preparation, sample dilution, and all steps involved in the sample analysis
24 process.

25 Alternative sampling methods will be considered for deployment. One option will be to use
26 subatmospheric samplers rather than pressurized sampling systems for stations VOC-A and
27 VOC-B. In addition, remote sensing by proposed draft EPA Method TO-16, open-path fourier
28 transform infrared spectrometry (**FTIR**) and extractive FTIR, may constitute supplemental or
29 alternative methods for detecting VOCs released from waste panels at WIPP. WIPP personnel
30 will continue to follow the development of emerging FTIR technology, and other potentially
31 applicable technologies for assessing VOCs in the WIPP environment. Real-time monitoring
32 with an FTIR system may be a feasible future option for the VOC Confirmatory Monitoring
33 Program. If the Permittees determine that an alternate sampling technique is appropriate, the
34 Permittees will submit a request for a Permit modification to the Secretary for review and
35 approval. The Permit modification request will include a revised confirmatory VOC monitoring
36 plan.

37 N-3d Sampling Schedule

38 The Permittees will evaluate whether the monitoring systems and analytical methods are
39 functioning properly. The assessment period will be determined by the Permittees.

40 Confirmatory VOC sampling at Stations VOC-A and VOC-B will begin with initial waste
41 emplacement in Panel 1. Sampling will continue until the certified closure of the last
42 Underground HWDU. Routine sampling will be conducted two times per week.

1 N-3e Data Evaluation and Reporting

2 When the Permittees receive laboratory analytical data from an air sampling event, the data will
3 be validated as specified in Section N-5e. After obtaining validated data from an air sampling
4 event, the data will be evaluated to determine whether the VOC emissions from the
5 Underground HWDUs exceed the COCs. The COCs for each of the nine target VOCs are
6 presented in Table N-2. The values are presented in terms of micrograms per cubic meter
7 ($\mu\text{g}/\text{m}^3$) and ppbv.

8 The COCs were calculated assuming typical operational conditions for ventilation rates in the
9 mine. The typical operational conditions were assumed to be an overall mine ventilation rate of
10 425,000 standard cubic feet per minute and a flow rate through the E-300 Drift at Station VOC-A
11 of 130,000 standard cubic feet per minute.

12 Since the mine ventilation rates at the time the air samples are collected may be different than
13 the mine ventilation rates during typical operational conditions, the Permittees will measure
14 and/or record the overall mine ventilation rate and the ventilation rate in the E-300 Drift at
15 Station VOC-A that are in use during each sampling event. The Permittees shall also measure
16 and record temperature and pressure conditions during the sampling event to allow all
17 ventilation rates to be converted to standard flow rates.

18 If the air samples were collected under the typical mine ventilation rate conditions, then the
19 analytical data will be used without further manipulation. The concentration of each target VOC
20 detected at Station VOC-B will be subtracted from the concentration detected at Station VOC-A.
21 The resulting VOC concentration represents the concentration of VOCs being emitted from the
22 open and closed Underground HWDUs upstream of Station VOC-A (or the Underground HWDU
23 VOC emission concentration.)

24 If the air samples were not collected under typical mine ventilation rate operating conditions, the
25 air monitoring analytical results from both Station VOC-A and Station VOC-B will be normalized
26 to the typical operating conditions. This will be accomplished using the mine ventilation rates in
27 use during the sampling event and the following equation:

$$28 \quad NVOC_{AB} = VOC_{AB} * \left(\frac{425,000_{scfm} / 130,000_{scfm}}{V_{O \text{ scfm}} / V_{E-300 \text{ scfm}}} \right) \quad (N-1)$$

29 Where: $NVOC_{AB}$ = Normalized target VOC concentration from Stations
30 VOC-A or VOC-B
31 VOC_{AB} = Concentration of the target VOC detected at Station VOC-A or
32 VOC-B under non-typical mine ventilation rates
33 scfm = Standard cubic feet per minute
34 V_o = Sampling event overall mine ventilation rate (in standard
35 cubic feet per minute)
36 VE-300 = Sampling event mine ventilation rate through the E-300
37 Drift (in standard cubic feet per minute)

1 The normalized concentration of each target VOC detected at Station VOC-B will be subtracted
2 from the normalized concentration detected at Station VOC-A. The resulting concentration
3 represents the Underground HWDU VOC emission concentration.

4 The Underground HWDU VOC emission concentration for each target VOC that is calculated for
5 each sampling event will be compared directly to its COC listed in Table N-2. This will establish
6 whether any of the concentrations of VOCs in the emissions from the Underground HWDUs
7 exceeded the COCs at the time of the sampling.

8 As specified in Permit Module IV, the Permittees shall notify the Secretary in writing, within five
9 (5) working days of obtaining validated analytical results, whenever the concentrations of any
10 target VOC listed in exceeds the concentration of concern specified in Table N-2.

11 The Underground HWDU VOC emission concentration for each target VOC that is calculated for
12 each sampling event will then be averaged with the Underground HWDU VOC emission
13 concentrations calculated for the air sampling events conducted during the previous 12 months.
14 This will be considered the running annual average concentration for each target VOC. For the
15 first year of air sampling, the running annual average concentration for each target VOC will be
16 calculated using all of the previously collected data.

17 As specified in Permit Module IV, the Permittees shall notify the Secretary in writing, within five
18 (5) working days of obtaining validated analytical results, whenever the running annual average
19 concentration (calculated after each sampling event) for any target VOC exceeds the
20 concentration of concern specified in Table N-2.

21 If the results obtained from an individual air sampling event do not trigger the notification
22 requirements of Permit Module IV, then the Permittees will maintain a database with the VOC
23 air sampling data and the results will be reported to the Secretary as specified in Permit Module
24 IV.

25 N-4 Sampling and Analysis Procedures

26 This section describes the equipment and procedures that will be implemented during sample
27 collection and analysis activities for VOCs at WIPP.

28 N-4a Sampling Equipment

29 The sampling equipment that will be used includes the following: 6-liter (L) stainless-steel
30 SUMMA[®] canisters, and VOC canister samplers. A discussion of each of these items is
31 presented below.

32 N-4a(1) SUMMA[®] Canisters

33 Six-liter, stainless-steel canisters with SUMMA[®] passivated interior surfaces will be used to
34 collect and store all ambient air and gas samples for VOC analyses collected as part of the
35 monitoring processes. These canisters will be cleaned and certified prior to their use, in a
36 manner similar to that described by Compendium Method TO-14A and the draft EPA CLP-SOW
37 for Analysis of Ambient Air in Canisters (EPA, 1994). The canisters will be certified clean to

below the required reporting limits for the VOC analytical method for the target VOCs (see Table N-4). The vacuum of certified clean samplers will be verified at the sampler upon initiation of a sample cycle.

N-4a(2) Volatile Organic Compound Canister Samplers

A conceptual diagram of a VOC sample collection unit is provided in Figure N-2. Two such systems, located at monitoring Stations VOC-A and VOC-B, will be operational at the time waste disposal operations begin in Panel 1. The sampling system consists of a sample pump, flow controller, sample inlet, two inlet filters in series to remove particulate matter, vacuum/pressure gauge, electronic timer, inlet purge vent, two sampling ports, and sufficient collection canisters so that any delays attributed to laboratory turnaround time and canister cleaning and certification will not result in canister shortages. Knowledge of sampler flow rates and duration of sampling will allow calculation of sample volume. The set point flow rate will be verified before and after sample collection from the mass flow indication. Prior to their initial use and annually thereafter, the sample collection units will be tested and certified to demonstrate that they are free of contamination above the reporting limits of the VOC analytical method (see Section N-5). Ultra-high purity humidified zero air will be pumped through the inlet line and sampling unit and collected in previously certified canisters as sampler blanks for analysis. The cleaning and certification procedure is derived from concepts contained in the EPA Compendium Method TO-14A (EPA, 1997).

N-4b Sample Collection

Six-hour integrated samples will be collected on each sample day. Alternative sampling durations may be defined for experimental purposes. The VOC canister sampler at each location will sample ambient air on the same programmed schedule. The sample pump will be programmed to sample continuously over a six-hour period during the workday. The units will sample at a nominal flow rate of 33.3 actual milliliters per minute over a six-hour sample period. This schedule will yield a final sample volume of approximately 12 L. Flow rates and sampling duration may be modified as necessary for experimental purposes and to meet the data quality objectives.

Sample flow will be checked each sample day using an in-line mass flow controller. The flow controllers are initially factory-calibrated and specify a typical accuracy of better than 10 percent full scale. Additionally, each air flow controller is calibrated at a manufacturer-specified frequency using a National Institute of Standards and Testing (NIST) primary flow standard.

Upon initiation of waste disposal activities in Panel 1, samples will be collected twice each week (at Stations VOC-A and VOC-B). Samples collected at the panel locations should represent the same matrix type (i.e., elevated levels of salt aerosols). To verify the matrix similarity and assess field sampling precision, field duplicate samples will be collected (two canisters filled simultaneously by the same sampler) from each sampling station (Stations VOC-A and VOC-B) during the first sampling event and at an overall frequency of 5 percent thereafter (see Section N-5a).

1 N-4c Sample Management

2 Field sampling data sheets will be used to document the sampler conditions under which each
3 sample is collected. These data sheets have been developed specifically for VOC monitoring at
4 the WIPP facility. The individuals assigned to collect the specific samples will be required to fill
5 in all of the appropriate sample data and to maintain this record in sample logbooks. The
6 program team leader will review these forms for each sampling event.

7 All sample containers will be marked with identification at the time of collection of the sample. A
8 Request-for-Analysis Form (Figure N-3) will be completed to identify the sample canister
9 number(s), sample type and type of analysis requested.

10 All samples will be maintained, and shipped if necessary, at ambient temperatures. Collected
11 samples will be transported in appropriate containers. Prior to leaving the underground for
12 analysis, sample containers may undergo radiological screening. No potentially contaminated
13 samples or equipment will be transported to the surface. No samples will be accepted by the
14 receiving laboratory personnel unless they are properly labeled and sealed to ensure a tamper
15 free shipment.

16 An important component of the sampling program is a demonstration that collected samples
17 were obtained from the locations stated and that they reached the laboratory without alteration.
18 To satisfy this requirement, evidence of collection, shipment, laboratory receipt, and custody will
19 be documented with a completed Chain-of-Custody Form (Figure N-4). Chain-of-custody
20 procedures will be followed closely, and additional requirements imposed by the laboratory for
21 sample analysis will be included as necessary.

22 Individuals collecting samples will be responsible for the initiation of custody procedures. The
23 chain of custody will include documentation as to the canister certification, location of sampling
24 event, time, date, and individual handling the samples. Deviations from procedure will be
25 considered variances. Variances must be preapproved by the program manager and recorded
26 in the project files. Unintentional deviations, sampler malfunctions, and other problems are
27 nonconformances. Nonconformances must be documented and recorded in the project files. All
28 field logbooks/data sheets must be incorporated into WIPP's records management program.

29 N-4d Sampler Maintenance

30 Periodic maintenance for canister samplers and associated equipment will be performed during
31 each cleaning cycle. This maintenance will include, but not be limited to, replacement of
32 damaged or malfunctioning parts without compromising the integrity of the sampler, leak testing,
33 and instrument calibration. Additionally, complete spare units will be maintained on-site to
34 minimize downtime because of sampler malfunction. At a minimum, canister samplers will be
35 certified for cleanliness initially and annually thereafter, after any parts that are included in the
36 sample flow path are replaced, or any time analytical results indicate potential contamination. All
37 sample canisters will be certified prior to each usage.

1 N-4e Analytical Procedures

2 Analytical procedures used in the analysis of VOC samples from canisters are based on
3 concepts contained in Compendium Method TO-14A (EPA, 1997) and in the draft CLP-SOW for
4 Analysis of Ambient Air (EPA, 1994). The technical approach for canister sample analysis is
5 summarized below.

6 N-4e(1) Sample Preparation

7 Because canisters will be pressurized during the sampling procedure, laboratory pressurization
8 will not normally be necessary for analyses. Canister pressures will be verified by the laboratory
9 when they are received to confirm that significant losses did not take place during shipping and
10 storage.

11 N-4e(2) Analytical System Requirements

12 The GC/MS analytical system will consist of three major components: the sample introduction
13 system, the analyte separation system (**GC**), and the analyte detector system (**MS**).

- 14 ● Sample Introduction System for Canisters: This system may include a drying tube to
15 remove moisture from the gas stream. One or more cryogenic traps may be used to
16 focus and desorb trapped material. Transfer lines within the introduction unit will be
17 heated as necessary so that volatile compounds are not actively adsorbed. Valves and
18 solenoids will be heated and of a low dead volume type. The introduction system will
19 have an in-line mass flow controller. The introduction unit will be capable of introducing
20 internal standards directly into the sample flow path.
- 21 ● Analyte Separation: Analyte separation will be achieved by GC. The GC will be capable
22 of subambient temperature programming.
- 23 ● Detection System: Analyte detection will be accomplished by MS. The MS must be
24 capable of scanning from 35 to 300 mass-to-charge ratio in one second or less, using 70
25 electron-volt electron energy in the electron impact ionization mode, and produce a
26 mass spectrum which meets all the instrument performance acceptance criteria when 50
27 nanograms of 4-bromofluorobenzene (**BFB**) is analyzed. The MS must have a data
28 system capable of continuous acquisition and storage on machine readable media
29 storing all raw data, and a computer algorithm for analyte quantitation and forward library
30 searching. All raw and processed GC/MS data must be stored on magnetic tape or disk
31 and maintained as Lifetime Records (i.e., for the life of the confirmatory VOC monitoring
32 program plus six years).

33 N-4e(3) Standard Preparation

34 Primary analytical standards will be prepared by the laboratory from commercially available,
35 certified calibration gases. Alternatively, primary standards may be generated internally by the
36 laboratory. Primary standards of analytes that are gases at standard temperature and pressure
37 may be prepared internally in a static gas dilution bottle. For analytes that are liquid or solid at
38 standard temperature and pressure, a mixture may be made and loaded directly into a standard

preparation cylinder. These internally generated standards will be checked against EPA audit cylinders or other reference materials to verify the accuracy of their concentrations.

Primary standards will be prepared for the nine target compounds as well as the internal standards. Secondary standards used for instrument calibration will be prepared from dilution of the primary standards.

N-4e(4) Calibration Procedures

Prior to the analysis of a standard curve, the GC/MS system must undergo a mass calibration check. This check is performed by introducing 50 nanograms of BFB into the capillary column through the preconcentrator. The requirements (criteria) for relative ion abundances for BFB, listed in Table N-3, must be met before analyses may proceed. BFB requirements must be met for each 12 hours of operation.

Quantitative standards for the nine target analytes will be analyzed at five concentrations. These concentrations should define the linear range of the instrument for these nine compounds; however, if some nonlinearity exists, concentrations may be determined by curve fitting or physically plotting the data. One standard concentration shall be at or near a concentration corresponding to the required MRL for each target compound. Relative response factors will be generated for each target compound. These response factors must meet the requirements listed in Section N-5a(3). As discussed above, if low concentration standards do not meet the linearity requirement, a curve-fitting routine may be used. The method used to quantify the data must be reported with the analytical results. In addition, a single point calibration check will be performed for each 12 hours of analytical system operation.

N-4e(5) Library Searches

In every sample analyzed, a forward search of the NIST library of mass spectra for tentatively identified compounds must be performed for all chromatographic peaks greater than 10 percent of the nearest internal standard.

N-4e(6) Data Reporting

The laboratory will provide a data package that identifies and describes the sample analyzed, the analysis date, the analytical results, the QC check results and description of any unusual conditions encountered.

Sample target analyte concentrations will be quantified using the average relative response factor of the initial calibration standards and will be reported in ppbv. Non-target sample contaminants identified by NIST library searches will be reported as tentatively identified compounds, and concentration calculations will be based on the response of the nearest internal standard. The relative response factor used for quantitation, as well as copies of spectra with the library search results (purity and/or fit), will be submitted with the results. A table listing the run sequence with the corresponding internal standard area counts will be reported with the analytical results. A narrative describing any problems with sample analyses will be included. Any nonconformances must be included with the reporting of the data.

1 N-4f Laboratory Selection

2 Sample will be analyzed at the WIPP on-site analytical laboratory and/or at a suitable contract
3 analytical laboratory. Upon selection of an off-site contract laboratory, the Permittees will ensure
4 that procured services conform to specified requirements. These measures generally will
5 include one or more of the following: (1) evaluation of the supplier's capability to provide
6 services in accordance with requirements, including a history of providing similar services;
7 (2) evaluation of objective evidence of conformance, such as laboratory document submittals;
8 and (3) examination of delivered services.

9 If the WIPP on-site analytical laboratory is utilized to conduct the sample analyses, then
10 duplicate samples from each sampling station (Stations VOC-A and VOC-B) will be collected at
11 an overall frequency of 10 percent. The duplicate samples will be analyzed by an independent
12 off-site analytical laboratory (see Section N-5a).

13 N-4g Laboratory Procedures

14 Specific laboratories that perform analyses and sampler certification activities for the
15 Confirmatory VOC Monitoring Program are required to develop and maintain the following SOPs
16 as appropriate:

- 17 ● Canister cleaning and certification
- 18 ● Sampler cleaning and certification
- 19 ● Analyses of VOCs in SUMMA[®] canisters
- 20 ● Data QA and reporting

21 Analytical laboratories are required to maintain an internal program QA manual, and to develop
22 and prepare a Quality Assurance Project Plan (**QAPjP**) covering cleaning and certification of
23 canisters and laboratory analysis of canister samples.

24 N-5 Quality Assurance

25 The QA activities for the confirmatory VOC monitoring program will be conducted in accordance
26 with the document *EPA Requirements for Quality Assurance Project Plans for Environmental*
27 *Data Operations* (EPA, 1994), and the *Interim Guidelines and Specifications for Preparing*
28 *Quality Assurance Project Plans* (EPA, 1983). The QA criteria for the confirmatory VOC
29 monitoring program are listed in Table N-4. This section addresses the methods to be used to
30 evaluate the components of the measurement system and how this evaluation will be used to
31 assess data quality.

32 These data quality objectives are based on control criteria proposed by the EPA as presented in
33 the *CLP-SOW for the Volatile Organics Analysis of Ambient Air in Canisters* (EPA, 1994).

34 N-5a Quality Assurance Objectives for the Measurement of Precision, Accuracy, Sensitivity, and 35 Completeness

36 QA objectives for this plan will be defined in terms of the following data quality parameters.

Precision. For the duration of this program, precision will be defined and evaluated by the RPD values calculated between field duplicate samples and between laboratory duplicate samples.

$$RPD = \left(\frac{(A-B)}{(A+B)/2} \right) * 100 \quad (N-2)$$

where: A = Original sample result
 B = Duplicate sample result

Accuracy. Analytical accuracy will be defined and evaluated through the use of analytical standards. Because recovery standards cannot reliably be added to the sampling stream, overall system accuracy will be based on analytical instrument performance evaluation criteria. These criteria will include performance verification for instrument calibrations, laboratory control samples, sample surrogate recoveries, and sample internal standard areas. These criteria will constitute the verification of accuracy for target analyte quantitation (i.e., quantitative accuracy). Evaluation of standard ion abundance criteria for BFB will be used to evaluate the accuracy of the analytical system in the identification of targeted analytes, as well as the evaluation of unknown contaminants (i.e., qualitative accuracy).

Sensitivity. Sensitivity will be defined by the required MRLs for the program. Attainment of required MRLs will be verified by the performance of statistical method detection limit (**MDL**) studies in accordance with 40 *Code of Federal Regulations* § 136. The MDL represents the minimum concentration that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. An MDL study will be performed by the program analytical laboratory prior to sampling and analysis, and annually thereafter.

Completeness. Completeness will be defined as the percentage of the ratio of the number of valid sample results received (i.e., those which meet data quality objectives) versus the total number of samples collected. Completeness may be affected, for example, by sample loss or destruction during shipping, by laboratory sample handling errors, or by rejection of analytical data during data validation.

N-5a(1) Evaluation of Laboratory Precision

Laboratory sample duplicates and blank spike/blank spike duplicates (**BS/BSD**) will be used to evaluate laboratory precision. QA objectives for laboratory precision are listed in Table N-4, and are based on precision criteria proposed by the EPA for canister sampling programs (EPA, 1994). These values will be appropriate for the evaluation of samples with little or no matrix effects. Because of the potentially high level of salt-type aerosols in the WIPP underground environment, the analytical precision achieved for WIPP samples may vary with respect to the EPA criteria. RPDs for BS/BSD analyses will be tracked through the use of control charts. RPDs obtained for laboratory sample duplicates will be compared to those obtained for BS/BSDs to ascertain any sample matrix effects on analytical precision. BS/BSDs and laboratory sample duplicates will be analyzed at a frequency of 10 percent, or one per analytical lot, whichever is more frequent.

1 N-5a(2) Evaluation of Field Precision

2 Field duplicate samples will be collected at a frequency of 5 percent for both monitoring
3 locations. The data quality objective for field precision is 35 percent for each set of duplicate
4 samples.

5 N-5a(3) Evaluation of Laboratory Accuracy

6 **Quantitative Accuracy.** Quantitative analytical accuracy will be evaluated through performance
7 criteria on the basis of (1) relative response factors generated during instrument calibration,
8 (2) analysis of laboratory control samples (**LCS**), and (3) recovery of internal standard
9 compounds. The criteria for the initial calibration (5-point calibration) is ≤ 30 percent relative
10 standard deviation for target analytes. After the successful completion of the 5-point calibration,
11 it is sufficient to analyze only a midpoint standard for every 12 hours of operation. The midpoint
12 standard will pass a 30 percent difference acceptance criterion for each target compound before
13 sample analysis may begin.

14 A blank spike or LCS is an internal QC sample generated by the analytical laboratory by spiking
15 a standard air matrix (humid zero air) with a known amount of a certified reference gas. The
16 reference gas will contain the target VOCs at known concentrations. Percent recoveries for the
17 target VOCs will be calculated for each LCS relative to the reference concentrations. Objectives
18 for percent recovery are listed in Table, and are based on accuracy criteria proposed by the
19 EPA for canister sampling programs (EPA, 1994). LCSs will be analyzed at a frequency of
20 10 percent, or one per analytical lot, whichever is more frequent.

21 Internal standards will be introduced into each sample analyzed, and will be monitored as a
22 verification of stable instrument performance. In the absence of any unusual interferences,
23 areas should not change by more than 40 percent over a 12-hour period. Deviations larger than
24 40 percent are an indication of a potential instrument malfunction. If an internal standard area in
25 a given sample changes by more than 40 percent, the sample will be reanalyzed. If the
26 40 percent criterion is not achieved during the reanalysis, the instrument will undergo a
27 performance check and the midpoint standard will be reanalyzed to verify proper operation.
28 Response and recovery of internal standards will also be compared between samples, LCSs,
29 and calibration standards to identify any matrix effects on analytical accuracy.

30 **Qualitative Accuracy.** Qualitative accuracy in the identification of target VOCs will be
31 evaluated by the relative ion abundance criteria established for the internal standard compound
32 BFB. For each 12 hours of sample analysis, a 50-nanogram injection of BFB must be made,
33 and the requirements listed in Table N-3 will be met before the instrument may be used to
34 analyze samples.

35 N-5a(d) Evaluation of Sensitivity

36 The presence of aerosol salts in underground locations may affect the MDL of the samples
37 collected in those areas. The intake manifold of the sampling systems will be protected
38 sufficiently from the underground environment to minimize salt aerosol interference.

The MDL for each of the nine target compounds will be evaluated by the analytical laboratories before sampling begins. The initial and annual MDL evaluation will be performed in accordance with 40 *Code of Federal Regulations* § 136 and with EPA/530-SW-90-021, as revised and retitled, "Quality Assurance and Quality Control" (Chapter 1 of SW-846) (1996).

N-5a(e) Completeness

The expected completeness for this program is greater than or equal to 90 percent. Data completeness will be tracked monthly.

N-5b Sample Handling and Custody Procedures

Sample packaging, shipping, and custody procedures are addressed in Section N-4C.

N-5c Calibration Procedures and Frequency

Calibration procedures and frequencies for analytical instrumentation are listed in Section N-4e(4).

N-5d Analytical Procedures

The analytical procedures for the Confirmatory VOC Monitoring Program, which are based on the draft *CLP-SOW for Volatile Organics Analysis of Ambient Air in Canisters* (EPA, 1994) and EPA Method TO-14A (EPA, 1997), are outlined in Section N-4e.

N-5e Data Reduction, Validation, and Reporting

A dedicated logbook will be maintained by the operators. This logbook will contain documentation of all pertinent data for the sampling. Sample collection conditions, maintenance, and calibration activities will be included in this logbook. Additional data collected by other groups at WIPP, such as ventilation airflow, temperature, pressure, etc., will be obtained to document the sampling conditions.

Data validation procedures will include at a minimum, a check of all field data forms and sampling logbooks will be checked for completeness and correctness. Sample custody and analysis records will be reviewed routinely by the QA officer and the laboratory supervisor.

Data will be reported as specified in Section N-3(e) and Permit Module IV.

Acceptable data for this monitoring program will meet stated precision and accuracy criteria. The QA objectives for precision, accuracy, and completeness as shown in Table N-4 can be achieved when established methods of analyses are used as proposed in this plan and standard sample matrices are being assessed. However, because of the potential for the samples to contain high levels of salt-type aerosols, the degree to which the QA objectives for the program can be achieved is presently uncertain. The program data will be evaluated and QA objectives modified as necessary based on the results of the QC testing program. If the Permittees determine that alternate QA objectives are required, the Permittees will submit a request for a Permit modification to the Secretary for approval.

1 N-5f Performance and System Audits

2 System audits will initially address start-up functions for each phase of the project. These audits
3 will consist of on-site evaluation of materials and equipment, review of canister and sampler
4 certification, review of laboratory qualification and operation and, at the request of the QA
5 officer, an on-site audit of the laboratory facilities. The function of the system audit is to verify
6 that the requirements in this plan have been met prior to initiating the program. System audits
7 will be performed at or shortly after to the initiation of the monitoring program and on an annual
8 basis thereafter.

9 Performance audits will be accomplished as necessary through the evaluation of analytical QC
10 data by performing periodic site audits throughout the duration of the project, and through the
11 introduction of third-party audit cylinders (laboratory blinds) into the analytical sampling stream.
12 Performance audits will also include a surveillance/review of data associated with canister and
13 sampler certification, a project-specific technical audit of field operations, and a laboratory
14 performance audit. Field logs, logbooks, and data sheets will be reviewed weekly. Blind-audit
15 canisters will be introduced once during the sampling period. Details concerning scheduling,
16 personnel, and data quality evaluation are addressed in the QAPjP.

17 N-5g Preventive Maintenance

18 Sampler maintenance is described briefly in Section N-4d Maintenance of analytical equipment
19 will be addressed in the analytical SOP.

20 N-5h Corrective Actions

21 If the required completeness of valid data (90 percent) is not maintained, corrective action may
22 be required. Corrective action for field sampling activities may include recertification and
23 cleaning of samplers, reanalysis of samples, additional training of personnel, modification to
24 field and laboratory procedures, and recalibration of test equipment.

25 Laboratory corrective actions may be required to maintain data quality. The laboratory
26 continuing calibration criteria indicate the relative response factor for the midpoint standard will
27 be less than 30 percent different from the mean relative response factor for the initial calibration.
28 Differences greater than 30 percent will require recalibration of the instrument before samples
29 can be analyzed. If the internal standard areas in a sample change by more than 40 percent,
30 the sample will be reanalyzed. If the 40 percent criterion is not achieved during the reanalysis,
31 the instrument will undergo a performance check and the midpoint standard reanalyzed to verify
32 proper operation. Deviations larger than 40 percent are an indication of potential instrument
33 malfunction.

34 The laboratory results for samples, duplicate analyses, LCSs, and blanks should routinely be
35 within the QC limits. If results exceed control limits, the reason for the nonconformances and
36 appropriate corrective action must be identified and implemented.

1 **N-5i Records Management**

2 The Confirmatory VOC Monitoring Program will require administration of record files (both
3 laboratory and field data collection files). The records control systems will provide adequate
4 control and retention for program-related information. Records administration, including QA
5 records, will be conducted in accordance with applicable DOE, MOC, and WIPP requirements.

6 Unless otherwise specified, monitoring program records will be retained as permanent records.
7 Temporary and permanent storage of QA records will occur in facilities that prevent damage
8 from temperature, fire, moisture, pressure, excessive light, and electromagnetic fields. Access
9 to stored Confirmatory VOC Monitoring Program QA Records will be controlled and documented
10 to prevent unauthorized use or alteration of completed records.

11 Revisions to completed records (i.e., as a result of audits or data validation procedures) may be
12 made only with the approval of the responsible program manager and in accordance with
13 applicable QA procedures. Original and duplicate or backup records of project activities will be
14 maintained at the WIPP site. Documentation will be available for inspection by internal and
15 external auditors.

1 N-6 References

2 U.S. Department of Energy. 1997. *Resource Conservation and Recovery Act Part B Permit*
3 *Application, Waste Isolation Pilot Plant (WIPP)*, Carlsbad New Mexico, Re. 6.4, 1997

4 U.S. Environmental Protection Agency. 1983. *Interim Guidelines and Specifications for*
5 *Preparing Quality Assurance Project Plans*. QAMS-005/80, EPA-600/4-83-004

6 U.S. Environmental Protection Agency. 1994. *Draft Contract Laboratory Program Statement of*
7 *Work, Volatile Organics Analysis of Ambient Air in Canisters*, EPA 540/R-94-085, December
8 1994, Washington, D.C.

9 U.S. Environmental Protection Agency. 1994. EPA QA/R-5, *Draft Interim Final, EPA*
10 *Requirements for Quality Assurance Project Plans for Environmental Data Operations*,
11 Washington, D.C.

12 U.S. Environmental Protection Agency. 1996. SW-846, *Test Methods for Evaluating Solid*
13 *Waste, Physical/Chemical Methods*. 3rd Edition. Office of Solid Waste and Emergency
14 Response, Washington, D.C.

15 U.S. Environmental Protection Agency. 1997. *Compendium Method TO-14A: Determination of*
16 *Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With*
17 *Subsequent Analysis By Gas Chromatography*, EPA 625/R-96/010b. Center for Environmental
18 Research Information, Office of Research and Development, Cincinnati, OH, January 1997.

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TABLES

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Table N-1
Target Analytes for Confirmatory VOC Monitoring During the WIPP Disposal Phase

Target Analyte	Common Synonyms and Acronyms	Chemical	Molecular Weight (g/mol)	Boiling Point (°C)*
Carbon tetrachloride	Tetrachloromethane	CCl_4	153.8	77
Chlorobenzene	Monochlorobenzene, Benzene chloride	$\text{C}_6\text{H}_5\text{Cl}$	112.6	132
Chloroform	Trichloromethane	CHCl_3	119.4	61
1,1-Dichloroethylene	1,1-Dichloroethene, Vinylidene chloride, 1,1-DCE	$\text{C}_2\text{H}_2\text{Cl}_2$	96.95	31
1,2-Dichloroethane	1,2-DCA, DCA, Ethylene dichloride, EDC, sym-Dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$	98.96	83
Methylene chloride	Dichloromethane	CH_2Cl_2	84.94	40
1,1,2,2-Tetrachloroethane	sym-Tetrachloroethane, Tetrachloroethane	$\text{C}_2\text{H}_2\text{Cl}_4$	167.9	147
Toluene	Methyl benzene	C_7H_8	92.13	111
1,1,1-Trichloroethane	1,1,1-TCA, TCA, Methyl chloroform	$\text{C}_2\text{H}_3\text{Cl}_3$	133.42	74

g/mol grams per mole
°C Degrees Celsius

* Handbook of Chemistry and Physics, 62nd Edition, CRC Press, 1982

Table N-2
Volatile Organic Compound Concentrations of Concern*

Compound	Molecular Weight (g/mol)	Drift E-300 Concentration	
		$\mu\text{g}/\text{m}^3$	ppbv
Carbon tetrachloride	153.8	1050	165
Chlorobenzene	112.6	1015	220
Chloroform	119.4	890	180
1,1-Dichloroethylene	96.95	410	100
1,2,-Dichloroethane	98.96	175	45
Methylene chloride	84.94	6700	1930
1,1,2,2-Tetrachloroethane	167.9	350	50
Toluene	92.13	715	190
1,1,1-Trichloroethane	133.42	3200	590

$\mu\text{g}/\text{m}^3$ micrograms per cubic meter
 ppbv parts per billion by volume

* Calculated at 25 degrees Celsius and 760 millimeters of mercury.

Table N-3
Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	8 to 40 percent of mass 95
75	30 to 66 percent of mass 95
95	Base Peak, 100 percent Relative Abundance
96	5 to 9 percent of mass 95
173	<2 percent of mass 174
174	50 to 120 percent of mass 95
175	4 to 9 percent of mass 174
176	93 to 101 percent of mass 174
177	5 to 9 percent of mass 176

Table N-4
Quality Assurance Objectives for Accuracy, Precision, Sensitivity,
and Completeness

Compound	Accuracy (Percent Recovery)	Precision (RPD) Laboratory Field		Required MRL (ppbv)	Completeness (Percent)
Carbon tetrachloride	60 to 140	25	35	2	90
Chlorobenzene	60 to 140	25	35	2	90
Chloroform	60 to 140	25	35	2	90
1,1-Dichloroethylene	60 to 140	25	35	5	90
1,2-Dichloroethane	60 to 140	25	35	2	90
Methylene chloride	60 to 140	25	35	5	90
1,1,2,2-Tetrachloroethane	60 to 140	25	35	2	90
Toluene	60 to 140	25	35	5	90
1,1,1-Trichloroethane	60 to 140	25	35	5	90

MRL method reporting limit

RPD relative percent difference

1

FIGURES

1

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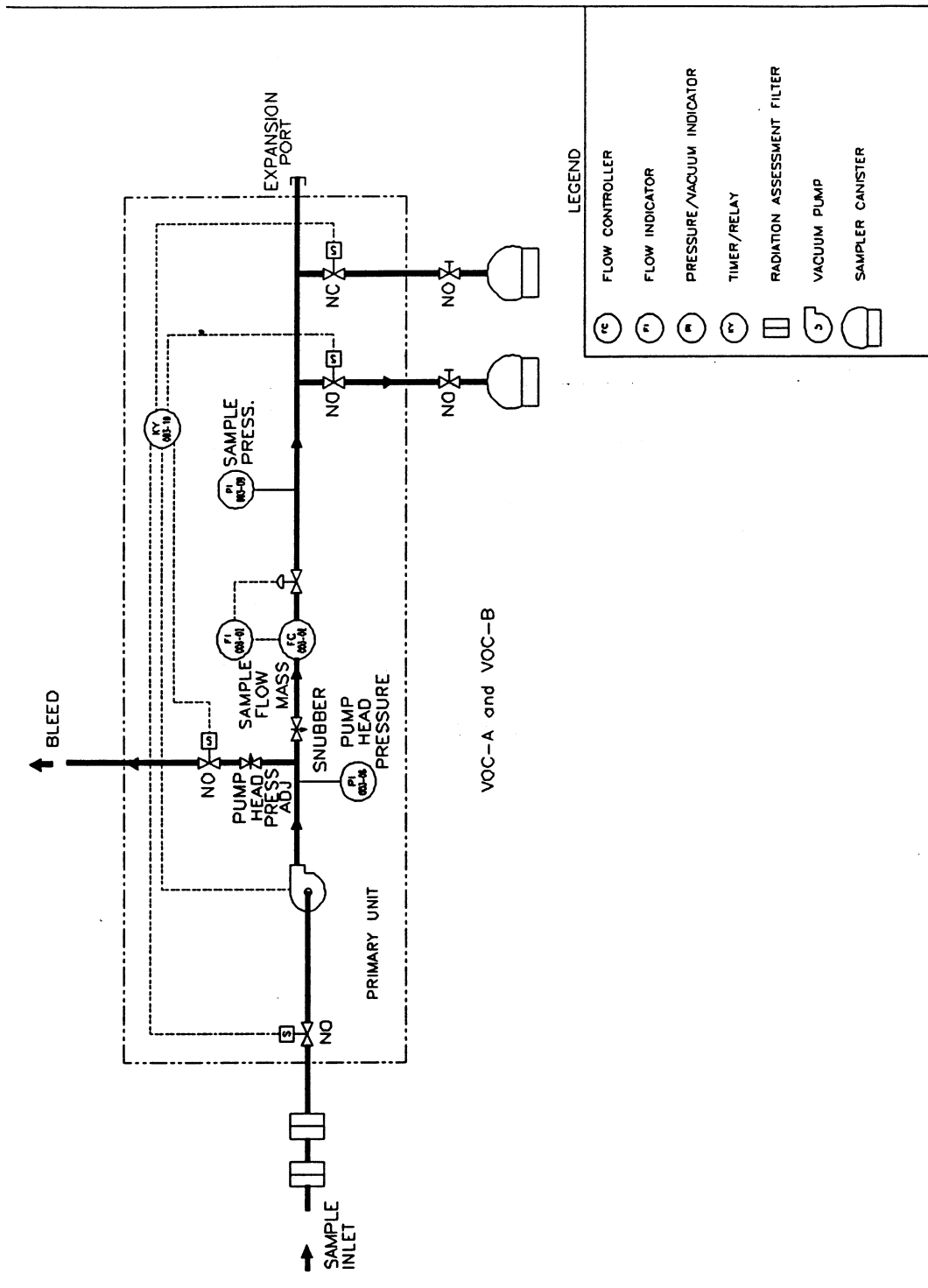


Figure N-2
VOC Monitoring System Design

REQUEST FOR ANALYSIS

{MOC Name and Address} _____

R/A Control _____
 C/C Control No. _____
 Date Sample Shipped _____
 Lab Destination _____
 Laboratory Contact _____
 Send Lab Report To _____

VOC Monitoring Program _____

Purchase Order No. _____
 Date Report Required _____
 Project Contact _____
 Project Contact Phone No. _____

Serial No.	Sample No.	C-of-C No.	Sample Type	Sample Pressure	Preservative	Contract-Specific Testing	Special Instructions

TURNAROUND TIME REQUIRED: (Rush must be approved by appropriate Manager) NORMAL _____ RUSH _____ (Subject to rush surcharge)
 POSSIBLE HAZARD IDENTIFICATION: (Please indicate if sample(s) are hazardous materials and/or contain high levels of hazardous substances.)
 NONHAZARD _____ FLAMMABLE _____ SKIN IRRITANT _____ HIGHLY TOXIC _____ BIOLOGICAL _____ OTHER _____

SAMPLE DISPOSAL (Please indicate disposition of sample following analysis.) RETURN TO CLIENT _____ DISPOSAL BY LAB _____ (Please Specify)

FOR LAB USE ONLY
 RECEIVED BY _____ DATE/TIME _____

Figure N-3
Example Request for Analysis Form

Effective July 8, 2005